FINAL – SYNOPSIS OF THE Ph.D. THESIS TO BE SUBMITTED

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Title of the Thesis **"SYNTHESIS AND CATALYTIC ACTIVITIES OF PALLADIUM ION DOPED TiO_2 BASED CATALYSTS: EXPERIMENTAL AND DENSITY FUNCTIONAL THEORETICAL STUDIES"**

Name of the candidate	**Mr. Prasanna**
Name of the Guide	Dr. Usha K M Associate Professor, Department of Chemistry, University College, Mangalore – 575001
Date of Registration	**31/03/2018**
Registration number	MU/EXB/Ph. D./CR.75/Chem./2020-21/E.13
Place of Work	Talent Development Centre Indian Institute of Science, Kudapura Challakere campus, Chitradurga – 577536 Karnataka, India

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FINAL-SYNOPSIS

The science and technology of heterogeneous catalysis are the rapidly moving frontiers in the field of catalysis. The synthesis of ammonia, sulphuric acid, and nitric acid, the production of hydrogen, the control of exhaust emissions, methanol synthesis, and many organic syntheses are associated with heterogeneous catalysis. Metals, metal clusters, alloys, metal oxides, sulfides, solid acids, and bases have been used as catalysts for many catalytic reactions since the early days of heterogeneous catalysis. Among these catalysts, supported and unsupported metals have been regarded as more efficient catalysts for their usefulness in various catalytic reactions.

Generally, heterogeneous catalysis deals with the gas phase reaction over a solid catalyst. Here, at least one of the reactants must be attached on the surface of the catalyst for a significant period of time called chemisorption. If a catalyst holds the very weakly or very strongly, it is a poor catalytic in the reaction. Because the weakly interacting catalyst doesn't absorb at all and strongly interacting catalyst leads to the formation of the adduct with the reactant. So, a potential catalyst should be a compromise between too weak and too strong chemisorption.

In the H_2-TPR of metal substituted catalysts, the reduction peak was observed at a much lesser temperature than that of pure noble metal oxides.[1-5] The oxygen storage capacity is also very large in substituted metal oxides than pure CeO_2 and TiO_2. The catalytic activity in CO oxidation with Pt, Rh, Ru, and Pd catalysts is very high. Among the noble metals, Pd is the

cheapest and shows more activity in gas-phase reactions. Therefore, the synthesis, structure, and catalytic activity of Pd^{2+} ion substituted catalyst should be explored. The combined experimental and theoretical findings of Pd^{2+} substituted catalyst is explored in an introductory chapter and 5 working chapters are given below.

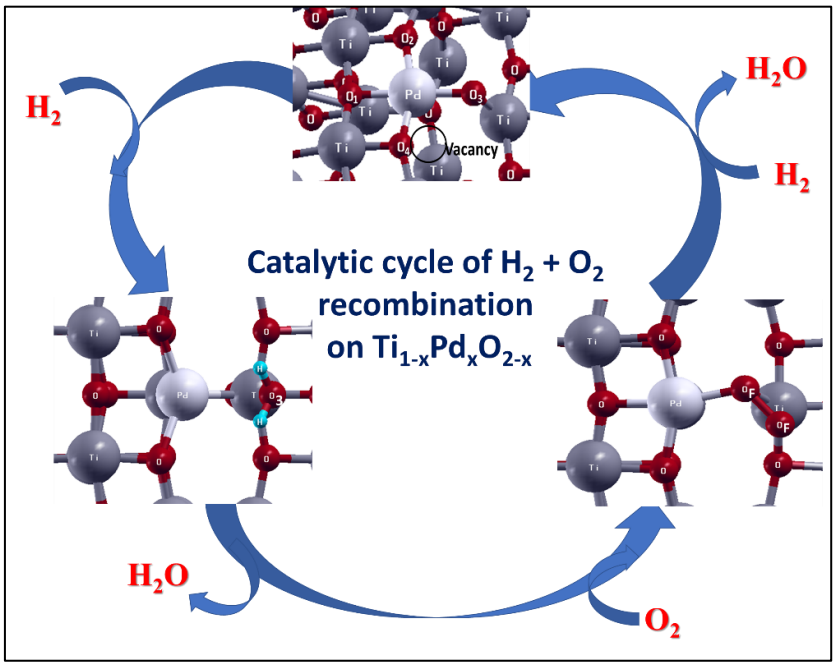
Chapter 1: A brief review of literature of metal ion substituted catalysts

The catalytic activities of various catalysts show that dissociated adsorption of CO and H_2 is important for CO oxidation and H_2+O_2 recombination. Noble metal-based catalysts are highly active in adsorption. The utility of heterogeneous catalysts in organic reactions is very effective in terms of recyclability. For that, catalyst coated cordierite monolith is used as the catalyst cartridge. Among all the noble metals Pd is the cheapest and most highly active catalyst. So, the activity of Pd^{2+} ion substituted catalyst in gas phase reaction such as H_2+O_2 recombination and organic reactions such as C-C coupling, alcohol oxidation, nitroreduction, and phenol formation explored in the working chapters.

Chapter 2: Lattice and feed oxygen exchange for the high rate of H_2 + O_2 recombination on $Ti_{1-x}Pd_xO_{2-x}$ catalyst at room temperature

The Pd ion substituted TiO_2, synthesized by solution combustion method crystallizes in anatase structure with stable composition $Ti_{1-x}Pd_xO_{2-x}$ creating an oxide ion vacancy per Pd^{2+} ion substitution. Over 1.35 moles of H_2 per mole of bulk Pd ions are adsorbed on the 5 nm catalyst crystalline which translates to over 4.5 moles of H_2 per mole of surface Pd ion. Pd ion substitution activates lattice oxygen in the catalyst leading to the formation of H_2O on exposure to H_2 gas at room temperature and on heating the reduced catalyst in the air at 350°C, the catalyst regenerates. A high rate of H_2+O_2 recombination up to 9 $\mu moles^{-1}g^{-1}$ was observed at room temperature over this catalyst. Extensive DFT calculation on (101) surface in $Ti_{31}Pd_1O_{63}$

slab confirmed (a) 3 out of 4 oxygen bonded to Pd forming nearly square planar local geometry are activated for H_2O formation; (b) dissociative adsorption of H_2 on one of the Pd-O bond; (c) exchange of feed oxygen and lattice oxygen during H_2+O_2 recombination cycle; (d) 2 H_2O molecules form per Pd ion per H_2+O_2 recombination cycle; (e) Pd ion undergoes redox cycle with Ti and oxide ions act as charge reservoirs.

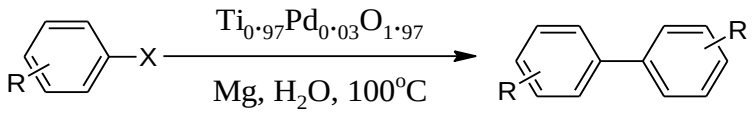


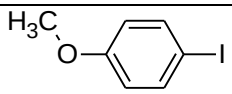
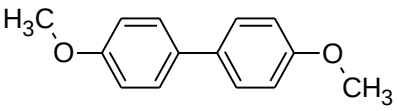
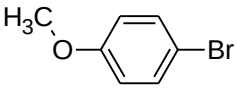
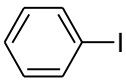
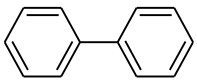
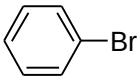
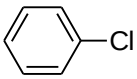
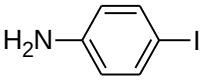
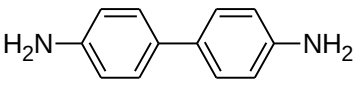
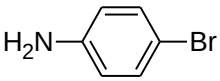
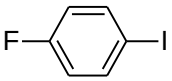
Chapter 3: Ligand and base free synthesis of biaryls from aryl halides in aqueous media with recyclable $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst

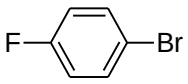
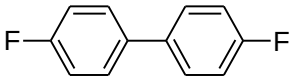
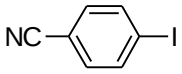
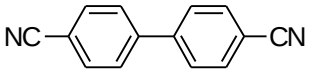
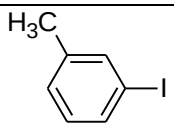
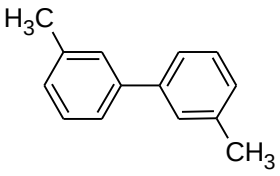
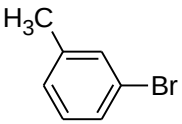
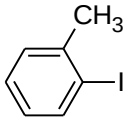
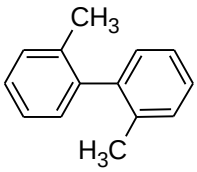
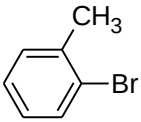
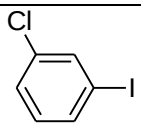
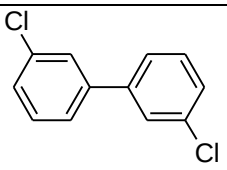
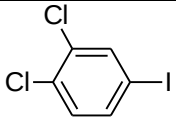
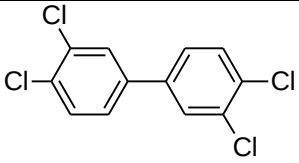
Facile protocol for the synthesis of biaryls from aryl halides in presence of magnesium metal without prior formation of organometallic intermediate has been exploited. Irrespective of the aqueous medium, $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst supports C-C bond formation reaction in presence of metals rather than dehalogenation without any additives. Homocoupling of 16 different aryl halides furnished corresponding biphenyls in good yield with better functional group tolerance. The recovery of the catalyst was carried out by employing catalyst coated cordierite monolith

up to the 7th cycle with high yields. A new approach for the cross-coupling reaction is also attempted.

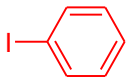
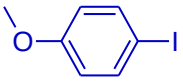
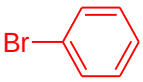
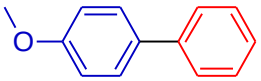
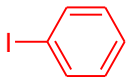
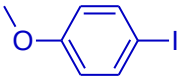
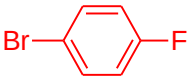
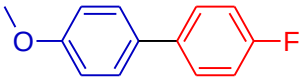
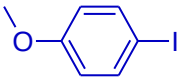
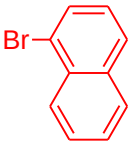
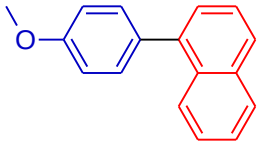
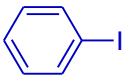
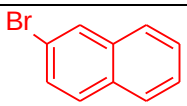
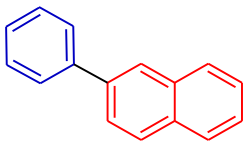
Scheme 1: Homocoupling of aryl halides with magnesium metal.



Entry	Substrate	Product	Time (h)	Yield
1			1	99
2			2	90
3			1.5	95
4			2	80
5			4.5	45
6			2	96
7			3.5	85
8			2	92

9			3	80
10			3	70
11			2.5	92
12			4	83
13			2.5	90
14			4.5	82
15			2	94
16			3	93

Scheme 2: Cross-coupling reaction of aryl halides.

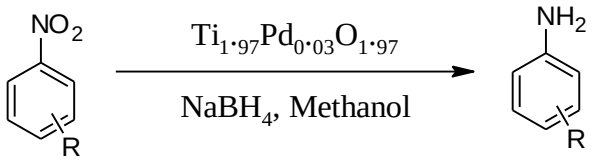
Entry	Aryl halides		Product	Time (h)	Yield (%)
1				1	50
2				1	96
3				1.5	94
4				1	95
5				2	94
6				1	60
7				1.5	62

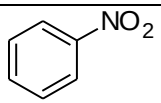
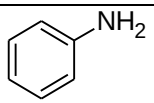
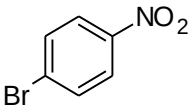
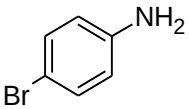
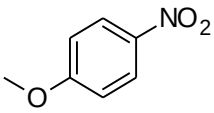
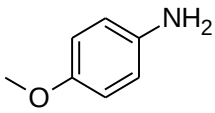
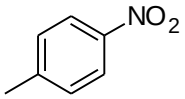
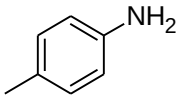
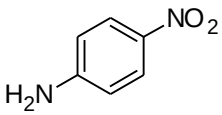
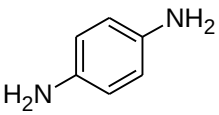
Chapter 4: Highly recyclable 3%Pd/TiO_2 catalyst for the potential reduction of aromatic nitroarenes

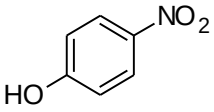
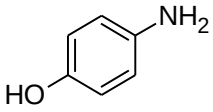
From the DFT study of the Pd substituted catalyst, there will be an oxide vacancy connected to the Pd^{2+} ion which is responsible for the redox behavior of the catalyst. In this chapter, we

report an efficient reduction of various nitro compounds in a short reaction time. The solvent-free reduction of the aromatic nitro compounds is also carried with H_2 gas in presence of Pd^{2+} substituted catalyst. Rapid reduction of the 4-nitrophenol can also be achieved with a very high apparent rate constant value of 70.48 x 10^{-3} s^{-1}. Recycling of the catalyst is carried out by employing a catalyst cartridge up to 10 cycles with ease.

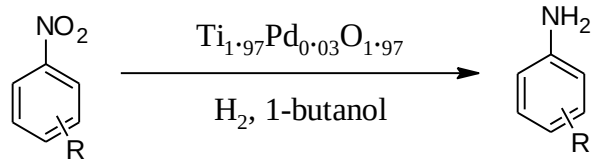
Scheme 3: : Reduction of various aromatic nitro compounds with $NaBH_4$ as the reducing agent.

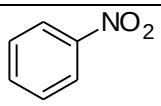
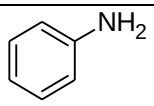
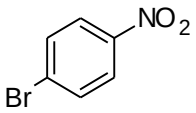
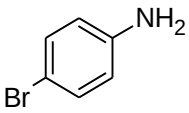
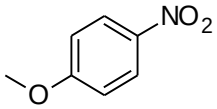
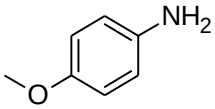
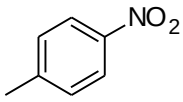
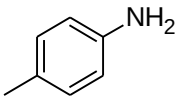
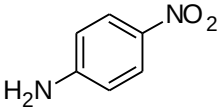
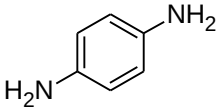
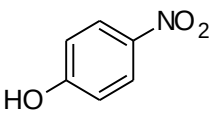
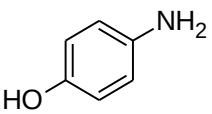


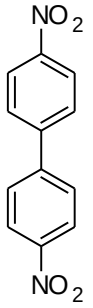
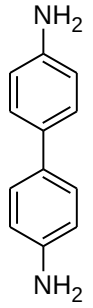
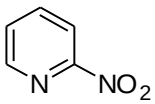
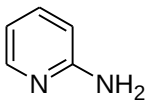
Entry	Nitro compound	Amine	Time (min)	Yield	TOF (h^{-1})
1.			5	92	6492
2.			10	89	3246
3.			10	90	3246
4.			10	88	3246
5.			15	91	2164

6.			20	84	1623

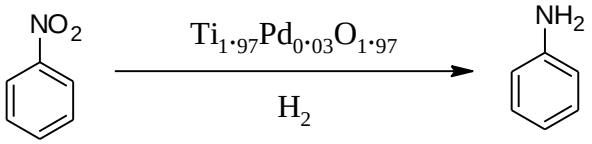
Scheme 4: Reduction of various aromatic nitro compounds with H_2 gas as the hydrogen source.



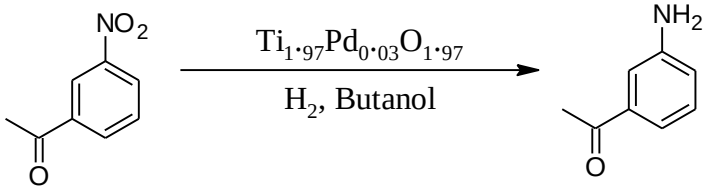
Entry	Nitro compound	Amine	Time (h)	Yield
1.			6	92
2.			6	87
3.			6	85
4.			6	88
5.			6	84
6.			6	81

7.			9	80
8.			6	81

Scheme 4: Solvent-free reduction of nitrobenzene with H_2 gas as the hydrogen source.



Scheme 5: Selectivity of nitro reduction in presence of carbonyl group.

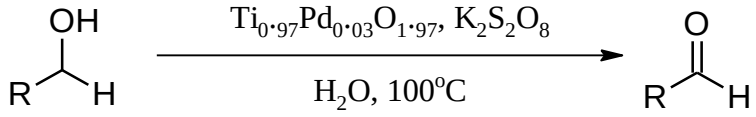


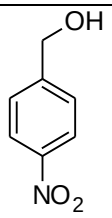
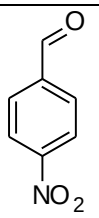
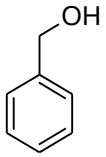
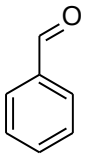
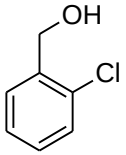
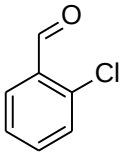
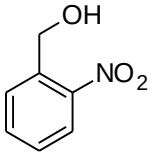
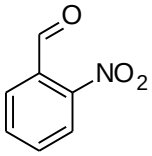
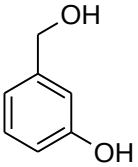
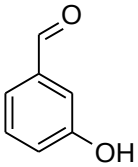
Chapter 5: Highly recyclable Palladium ion substituted TiO_2 catalyst for the efficient alcohol oxidation reaction

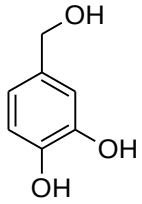
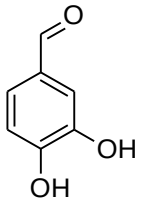
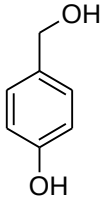
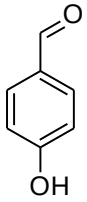
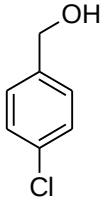
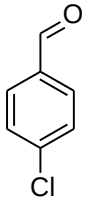
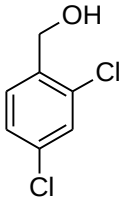
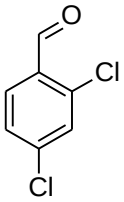
The catalysts containing noble metals are expensive. So, the recyclability of the catalyst is considerable in catalytic oxidation. The palladium ion dispersed TiO_2 based catalyst is efficient in alcohol oxidation, especially in benzylic oxidation also. This catalyst is synthesized by the solution combustion method with ease. In this study, we report efficient oxidation of diverse primary and secondary alcohols in a short reaction time. The selective oxidation of primary

alcohols proceeded furnishing aldehydes with good yields. Recycling of the catalyst is carried out by employing a catalyst cartridge up to 10 cycles.

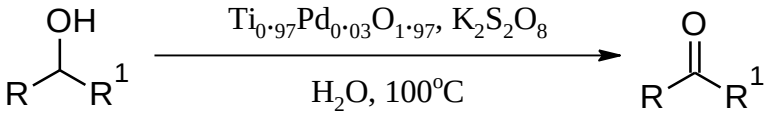
Scheme 6: Oxidation of primary alcohols.

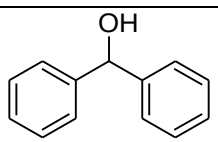
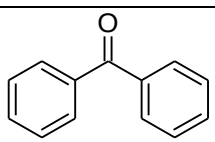


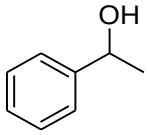
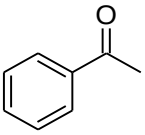
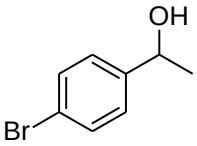
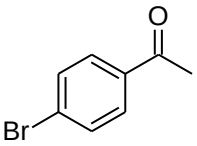
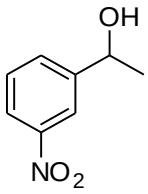
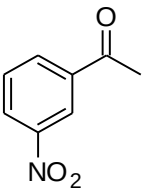
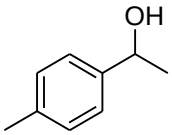
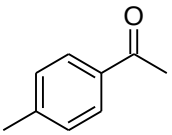
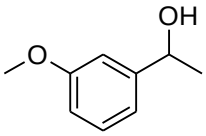
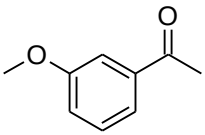
Entry	Substrate	Product	Percentage yield
1.			85
2.			90
3.			83
4.			80
5.			80

6.			78
7.			82
8.			87
9.			84

Scheme 7: Oxidation of secondary alcohols.



Entry	Substrate	Product	Percentage yield
1.			92

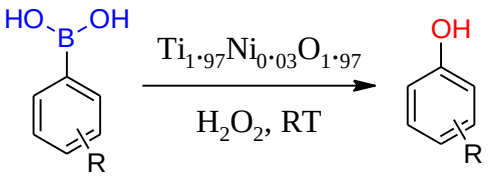
2.			93
3.			93
4.			91
5.			91
6.			90

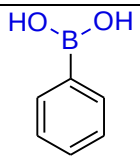
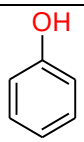
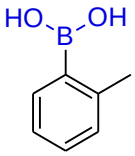
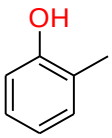
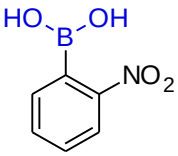
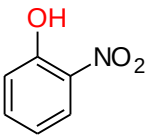
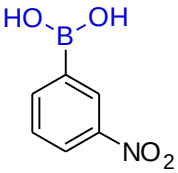
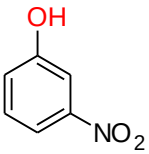
Chapter 6: Highly recyclable $Ti_{0.97}Ni_{0.03}O_{1.97}$ catalyst coated on cordierite monolith for efficient transformation of arylboronic acids to phenols and reduction of 4-nitrophenol

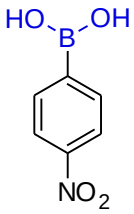
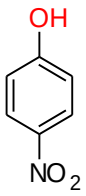
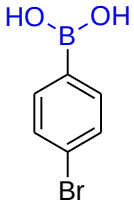
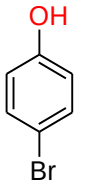
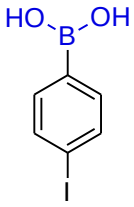
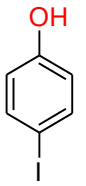
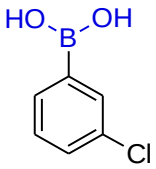
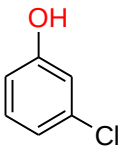
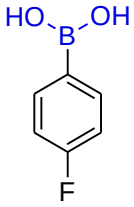
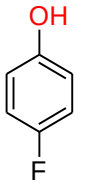
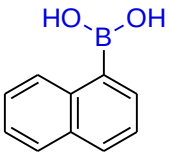
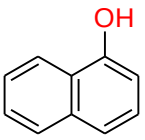
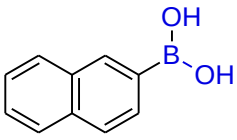
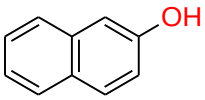
A stable Ni^{2+} substituted TiO_2 catalyst ($Ti_{0.97}Ni_{0.03}O_{1.97}$) has been synthesized by the solution combustion method with an average crystallite size of 7.5 nm. $Ti_{1-x}Ni_xO_{2-x}$ (x = 0.01 - 0.06) crystallize in TiO_2 anatase structure with Ni^{2+} substituted in Ti^{4+} ion sites and Ni takes a nearly square planar geometry. This catalyst is found to be highly active in the transformation of diverse arylboronic acids to corresponding phenols. The catalyst coated cordierite monolith can be recycled even up to 20 cycles with a cumulative TOF of $1.8 \times 10^5\ h^{-1}$. In scale-up

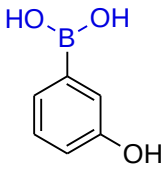
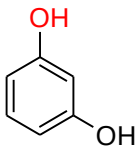
reactions, various phenols are synthesized by employing a single cordierite monolith. It also shows high performance in the reduction of 4-nitrophenol.

Scheme 8: *Ipso* hydroxylation of aryl boronic acid with $Ti_{0.97}Ni_{0.03}O_{1.97}$ catalyst.

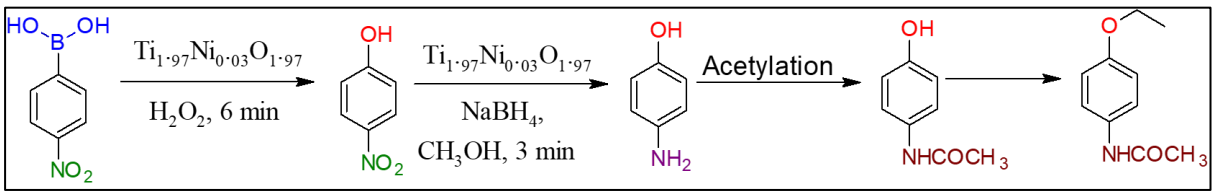


Entry	Reactant	Product	Time (min)	TOF (h^{-1})
1			2	8000
2			3	5333
3			8	2000
4			4	4000

5			6	2667
6			4	4000
7			3.5	4571
8			4	4000
9			3	5333
10			8	2000
11			8	2000

12			3.5	4571

Scheme 9: Synthetic application of $Ti_{0.97}Ni_{0.03}O_{1.97}$ catalyst in the synthesis of 4-AP.



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List of Publications

1. Ligand and Base Free Synthesis of Biaryls from Aryl Halides in Aqueous Media with Recyclable $Ti_{0.97}Pd_{0.03}O_{1.97}$ Catalyst, **Prasanna,** Shrikanth K. Bhat, K. M. Usha, M. S. Hegde, Catalysis Letters (2021) 151:3313–3322, DOI: http://doi.org/10.1007/s10562-021-03560-5.
2. Highly recyclable $Ti_{0.97}Ni_{0.03}O_{1.97}$ catalyst coated on cordierite monolith for efficient transformation of arylboronic acids to phenols and reduction of 4-nitrophenol, **Prasanna**, K. M. Usha, M. S. Hegde, Dalton Transactions, 2021, 50, 14223. DOI: http://doi.org/10.1039/d1dt02293h.
3. Highly recyclable palladium ion substituted TiO_2 as the versatile ligand-free catalyst for efficient alcohol oxidation and reduction of aromatic nitro compounds, **Prasanna,** K M Usha, Journal of Chemical Sciences, 2022 (Accepted).
4. Lattice oxygen and feed oxygen exchange for the high rate of H_2+O_2 recombination on $Ti_{1-x}Pd_xO_{2-x}$ catalyst at room temperature, **Prasanna**, K. M. Usha, Manish Jain, M. S. Hegde, Catalysis Letters, 2022 (Under review).
5. Formation and Structure of Iodine: Water (H_2O-I_2) charge-transfer complex, **Prasanna**, Shrikanth K. Bhat, M. S. Hegde, Journal of Chemical Sciences, 2021, 133:51. DOI: https://doi.org/10.1007/s12039-021-01912-7.
6. Palladium Ion Catalysed Oxidative C–C Bond Formation Reactions in Arylboronic Acid: Application of Cordierite Monolith Coated Catalyst, Shrikanth K. Bhat, **Prasanna,** Jagadeesh Prasad Dasappa, M. S. Hegde, Catalysis Letters, 2020, 150:2911–2927. DOI: https://doi.org/10.1007/s10562-020-03194-z.
7. An efficient $Ti_{0.95}Cu_{0.05}O_{1.95}$ catalyst for ipso – hydroxylation of arylboronic acid and reduction of 4-nitrophenol, Shrikanth K. Bhat, **Prasanna**, Jagadeesh Prasad Dasappa, M.

S. Hegde, Journal of Chemical Sciences, 2021, 133:84. DOI: https://doi.org/10.1007/s12039-021-01933-2.

Papers Presented in International Conferences

1. **Prasanna,** K. M. Usha, M. S. Hegde, Palladium substituted TiO_2 coated on cordierite monolith for solvent-free reduction of aromatic nitro compounds, presented at two days international conference on "Current trends in advanced chemistry" organized by the Department of Chemistry, Saranathan College of Engineering, Trichy-12 on 20th and 21st September 2021.
2. **Prasanna,** K. M. Usha, M. S. Hegde, Nickel substituted TiO_2 coated on cordierite monolith for efficient transformation of aryl boronic acids to phenols, presented at three days international conference on "Frontiers in Chemistry" organized by School of Applied Sciences, Department of Chemistry, Reva University, Bangaluru on 21st to 23rd October 2021.
3. **Prasanna,** K. M. Usha, M. S. Hegde, Ionic palladium substituted TiO_2 catalyst coated on cordierite monolith is a highly recyclable catalyst for the rapid reduction of 4-nitrophenol, presented at three days international conference on "Advanced Materials And Mechanical Characterization" organized by Department of Physics and Nanotechnology and Department of Mechanical Engineering, SRM Institute Of Science And Technology, Tamil Nadu on 2nd to 4th December 2021.

Prasanna **Dr. Usha K M**

(Student) (Guide)